X-ray excited Auger transitions of Pu compounds

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Abstract

X-ray excited Pu core-valence-valence and core-core-valence Auger line-shapes were used in combination with the Pu 4f photoelectron peaks to characterize differences in the oxidation state and f electron localization for Pu compounds. The evolution of the Pu 4f core-level chemical shift as a function of sputtering depth profiling and hydrogen exposure at ambient temperature was quantified. The combination of the Auger peak energies with the associated chemical shift of the Pu 4f photoelectron line defines the Auger parameter and results in a reliable method for definitively determining oxidation states independent of binding energy calibration. Results show that PuO_2, Pu_2O_3, $PuH_{2.7}$ and Pu have definitive Auger line-shapes. These data were used to produce a chemical state (Wagner) plot for select plutonium oxides. This Wagner plot allowed us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu 4f binding energy alone.

INTRODUCTION

Oxidation/reduction reactions on plutonium metal continue to garner interest for establishing safe handling and storage procedures. X-ray photoelectron spectroscopy (XPS) has long been used to provide information on oxidation state, chemical environment, and bonding characteristics of plutonium surfaces. XPS core-level chemical shifts have established that the stable oxides of Pu are plutonium sesquioxide (Pu_2O_3, O/Pu = 1.5, Pu^{3+}) and plutonium dioxide (PuO_2, O/Pu = 2.0, Pu^{4+}), both semiconductors that typically form a layered structure on the surface of Pu metal. [1-6] However, core-level spectroscopy alone does not uniquely characterize the local chemical environment without proper energy calibration. By measuring the X-ray excited Auger transitions and combining with the core-level photoemission in a chemical state plot (Wagner plot), one can gain additional information on the initial state effects and final state relaxation energy. [7]

Employing Auger line-shape analysis of core-valence-valence (CVV) and core-core-valence (CCV) transitions in Pu and Pu oxides will further elucidate surface electronic structure, core-hole screening and hole-state localization. [8-13] Specifically, the Auger line width is indicative of core-hole screening and the intensity represents the degree of localization. In addition, comparing CVV to CCV transitions will aid in understanding the influence of the degree of f electron localization on oxidation/reduction processes. Note also that inclusion of O impurities leads to f-electron delocalization and this delocalization leads to Auger line-shapes that are strongly dependent on the nature of the Pu-O chemical bond, e.g. covalency.

This investigation combines XPS core-level spectra with X-ray excited Auger transitions to provide definitive information on oxidation state and f electron localization. The Pu 4f core-level and Auger CVV results are combined in Wagner plots and the Auger parameter (difference

in the binding energy of the photoelectron and Auger lines) is calculated in order to determine the utility of this technique in the analysis of plutonium alloys and compounds.

EXPERIMENTAL

XPS and X-ray excited Auger measurements were made using a Physical Electronics 5400 spectrometer employing achromatic Al Ka X-ray source (1486.7 eV) operating with a base pressure of 1 x 10^{-9} torr. All measurements were made with the sample surface normal to the electron analyzer unless otherwise stated. Spectra were acquired using a 0.2 eV step size and pass energy of 35.75 eV, giving an energy resolution of 0.5 eV that when combined with the 0.85 eV full width half maximum (FWHM) Al Kα line width gives a resolvable XPS peak width of 1.3 eV. No additional gains in spectral resolution were found acquiring spectra at lower pass energy values. Curve fitting of non-resolved core-level peaks and determination of the Auger peak position was accomplished using Multipak 9.2 (PHI). Curve fitting routines with asymmetric line-shapes and a Shirley background were used for the Pu 4f core-level. The CVV and CCV Auger peak position were determined by the minimum of the first derivative to resolve the Auger peaks from the inelastic background. For this study, the Pu Auger transitions of interest are the P_1VV with a kinetic energy between 78-82 eV and the $O_{4,5}$VV with kinetic energies between 96-103 eV. [14] Although less intense, the NOV Auger transition with a kinetic energy between 316-318 eV was also measured for comparison.

The samples studied were gallium stabilized δ-Pu alloy (≈ 0.6 $^w/_o$) having typical grain size of 30-50 μm. Sputter cleaning of the as received δ-Pu alloy was accomplished with 4.5 kV Ar^+ rastered over a broad 5 x 5 mm area giving an approximate sputter etch rate of ≈ 0.1 nm/min. Annealing of the sample was avoided to prevent bulk to surface segregation of any carbon

impurity. Hydrogen dosing of the sputter cleaned Pu metal was performed *in-situ* at 1 x 10^{-5} torr and ambient temperature and a total dose of 10200 L of H_2 (1 Langmuir = 1 x 10^{-6} torr-sec).

RESULTS AND DISCUSSION

The evolution of the Pu $4f_{7/2,5/2}$ spin-orbit pair during the sputter depth profiling of the oxide layers is presented in Figure 1. The Pu 4f spectrum for the surface is the lower trace having a Pu $4f_{7/2}$ peak binding energy of 426.2 eV with the satellite loss peak on the high binding energy side. Note that a small Pu^{3+} component is present in the curve fit that indicates incomplete PuO_2 coverage of the Pu_2O_3 on the unpolished Pu metal surface. As the sputter depth profiling proceeds, the Pu 4f peak shape changes from the distinct Pu^{4+} signature to that attributable to Pu^{3+} with a peak binding energy of 424.6 eV followed by a change to the substrate Pu^0 peak at binding energy 422.0 eV. [1-6] The sputter depth profile results indicate Pu oxides with diffuse interfaces as opposed to distinct oxide layers.

The core hole left by the 4f photoelectron can be filled by a 5d electron with a 5f electron emitted resulting in a $N_{6,7}O_{4,5}V$ Auger transition as shown in Figure 2. In addition to the observed chemical shifts, note the change in the N_7O_5V and N_6O_5V line widths and intensities as the Pu valence changes from Pu^{4+} through Pu^{3+} and finally to Pu^0. Since the Auger line width is indicative of core-hole screening and the intensity represents the degree of 5f localization, this CCV Auger transition reveals that the dioxide and sesquioxide have poorly screened core-holes and that the 5f electrons are delocalized in the dioxide.

Similar trends are observed in the CVV Auger transitions presented in Figure 3. Specifically, the P_1VV Auger transition representing a 6s photoelectron core hole filled by a 5f electron with another 5f electron emitted, and the $O_{4,5}VV$ Auger transitions representing 5d

photoelectron core holes filled by 5f electrons followed with emission of 5f Auger electrons. The P_1VV and $O_{4,5}VV$ Auger transitions have the lowest intensity for the dioxide, which reflects the fact that inclusion of O impurities, e.g. $PuO_{1.5}$ versus PuO_2, leads to f-electron delocalization. [13,15] This localization/delocalization transition of the f electrons affects the oxidation/reduction energetics. In addition, note that the OVV peaks transition from a broad single peak for the dioxide to a resolved doublet for the Pu metal. This is indicative of how covalency affects the OVV exchange splitting.

Table I presents the intensity ratios of CVV to CCV Auger transitions for each Pu ionic configuration. These intensity ratios increase as the ionic configuration moves from Pu^{4+} to Pu^{3+} to Pu^0. The P_1VV/N_7O_5V intensity ratio reveals a trend in the degree of 5f localization for each Pu oxidation state by comparing Auger transitions with initial 6s core-hole state versus initial 4f core-hole state. The O_4VV/N_7O_5V intensity ratio also contains information about the Pu 5d-O 2p hybridization for the oxides.

Applying this methodology of measuring Pu 4f core-level spectra in combination with X-ray excited PVV Auger spectra for a hydrogen-dosed surface of Pu yields a chemical state plot (Wagner plot). Figure 4 shows the Pu $4f_{7/2,5/2}$ core-level spectra for the sputter cleaned Pu before and after H_2 dosing and the associated Pu PVV spectra. The Wagner plot of the Pu PVV Auger transition and Pu $4f_{7/2}$ photoemission for select Pu compounds is presented in Figure 5. Note that Pu hydride ($PuH_{2.7}$) is considered to be trivalent with a ground state configuration of $5f^5$ (Pu^{3+}). [16] This Wagner plot allows us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu 4f binding energy alone.

CONCLUSIONS

X-ray core-level photoelectron spectroscopy was combined with X-ray excited Auger electron spectroscopy to characterize Pu oxidation state and f electron localization. The observed decreasing PVV and OVV line widths as the Pu ionicity changes from Pu^{4+} to Pu^{3+} to Pu^0 reveals poorly screened features for the oxides. In addition, the increasing intensity reveals the change in the degree of 5f localization. Also, X-ray excited CVV and CCV Auger line-shapes have definitive characteristics for PuO_2, Pu_2O_3, $PuH_{2.7}$ and Pu metal. X-ray induced Auger lines and combined with core-level shifts allows indirect detection of hydrides. Further characterization is of course necessary for full quantification.

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Table I. Comparison of CVV and CCV Auger intensities

Pu valence	P_1VV/N_7O_5V	O_4VV/N_7O_5V
Pu^{4+}	5.88	4.99
Pu^{3+}	6.55	5.24
Pu^0	6.92	5.86

Figure captions

Figure 1.	High-resolution Pu $4f_{7/2,5/2}$ core-level spectra versus sputter etch time showing change in valence through the oxide layers.

Figure 2.	X-ray excited Pu $N_{6,7}O_{4,5}V$ Auger transitions versus sputter etch time

Figure 3.	X-ray excited Pu PVV and OVV Auger transitions versus sputter etch time

Figure 4.	High-resolution Pu $4f_{7/2,5/2}$ core-level and X-ray excited PVV Auger transition versus hydrogen dosing at ambient temperature.

Figure 5.	Wagner plot of the Pu $4f_{7/2}$ photoemission binding energy and Pu P_1VV X-ray excited Auger electron kinetic energy for select Pu compounds.

Pu 4f$_{5/2}$

Pu 4f$_{7/2}$

10200L H$_2$

4800L H$_2$

Pu

Binding Energy (eV)

X-ray induced Auger Pu PVV

10200L H$_2$

4800L H$_2$

sputter clean

O$_4$VV

O$_5$VV

Binding Energy (eV)